# SYNOPSIS

# INVESTIGATION OF $(Bi_{1-x}Sb_x)_2S_3$ THIN FILMS AS PHOTOELECTRODES FOR ELECTROCHEMICAL PHOTOVOLTAIC CELLS


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# Investigation of $(Bi_{1-x}Sb_x)_2S_3$ Thin films as Photoelectrodes for Electrochemical Photovoltaic Cells

The successful commercialisation of photovoltaic cells as reliable source of energy is elusive because of major limiting factors such as high cost and low efficiency. Considerable efforts are being made to achieve remarkable efficiencies at a reasonable production cost. Electrochemical Photovoltaic Cells (ECPV) are cost effective alternatives for p-n junction solar cells. Though electrochemical photovoltaic cell is relatively cheaper than a p-n junction solar cell, conversion efficiency of ECPV is lower than its solid state counterpart. ECPV cells with enhanced conversion efficiencies would be a viable approach for the conversion of solar energy into electrical energy at lower cost. ECPV cell consists of a semiconductor electrode immersed in a suitable electrolyte with a counter electrode. Since the semiconductor electrode is the only active material involved in an ECPV cell, the performance of the cell can be improved by tailoring the properties of the semiconductor material. The identification of an appropriate material which can be used as an efficient photoelectrode for ECPV cell is a challenging task. And hence in the present work an attempt has been made to identify and explore the properties of a novel semiconductor material for electrochemical photovoltaic application.

The objectives of the present work are as follows.

- To identify a novel material for the preparation of photoelectrode
- To deposit device quality thin films of the material by a low cost technique
- To explore the structural, optical, electrical and photoelectrochemical properties of the material
- To form and study the characteristics of the electrochemical photovoltaic cell with the prepared photoelectrode

The work is systematically carried out in the following four phases.

**Phase 1**

a. Identification of a novel material for the preparation of photoelectrode
b. Identification of an appropriate technique for the deposition of thin films of the material

**Phase 2**

Deposition and Characterisation of $Bi_2S_3$ thin films

**Phase 3**

Deposition and Characterisation of $(Bi_{1-x}Sb_x)_2S_3$ thin films

**Phase 4**

Formation and Characterisation of electrochemical photovoltaic cell

**Organisation of the Thesis**

The thesis consists of seven chapters. The first chapter gives the introduction for the field of research and the motivation behind the present work. The important reports of the work already done in the area of the proposed work are presented in chapter two. The experimental techniques adopted for the deposition and characterisation of the thin films are given in chapter three. Chapter four and five deal with the deposition and characterization of the deposited $Bi_2S_3$ and $(Bi_{1-x}Sb_x)_2S_3$ thin films respectively. Details of the formation of electrochemical photovoltaic cell and the device characteristics are presented in chapter six. Major conclusions drawn from the present study are summarised in chapter seven.

## Phase 1

### a. Identification of novel material for the preparation of photoelectrode

The primary requirement for an electrochemical photovoltaic cell is that the photoelectrode should have a band gap in the range of 1.4-1.7 eV. [Suresh Chandra,1999] Bismuth trisulphide ($Bi_2S_3$) in thin film of is particularly a potential

material because of its band gap, absorption coefficient, reasonable conversion efficiency, stability together with low cost [Mane et al. 1999]. Reports are available on the properties of thin films deposited by conventional methods and also on the characteristics of ECPV cells formed with $Bi_2S_3$ as the active material [Biljano Pejova et al.1999, Benramdane et al. 1997, Rincon et al. 1998, Rincon et al.1999, Sonawane et al.2007, Ubale et al.2008]. It is well known that it is possible to alter the optical, electrical and photoelectrochemical properties of the material by forming ternary films with varying compositions. Antimony sulphide has similar crystallographic properties as that of $Bi_2S_3$ thereby suggesting the possibility of existence of $(Bi_{1-x}Sb_x)_2S_3$ thin films. Structural, optical, electrical and photoelectrochemical properties of the $(Bi_{1-x}Sb_x)_2S_3$ thin films with $0.01 \leq x \geq 0.1$ have not been reported till date. And hence in the present work an attempt has been made to investigate the properties of $(Bi_{1-x}Sb_x)_2S_3$ thin films for electrochemical photovoltaic application.

**b. Identification of an appropriate technique for the deposition of thin films of the material**

Properties of thin films are dependent on the method of deposition. Proper choice of the deposition technique for a particular material is crucial for obtaining high quality thin films. Chemical Spray Pyrolysis (CSP) is an efficient technique for the deposition of thin films. The microstructure of the film deposited by spray pyrolysis depends very sensitively on the size of the droplets besides other parameters such as spray head geometry, carrier gas, liquid flow pattern and rate, droplet velocities and geometries, nature and temperature of the substrate. Improved microstructure of the film may lead to enhanced properties of the films. The microstructure of the films deposited by CSP can be influenced by the proper choice of the above said parameters. In the present work conventional atomizer is replaced by a nebulizer which is capable of producing very fine and uniform droplets of the solution to be sprayed. The spray gun for the nebulizer is indigenously made and the dimensions and geometry of the spray gun are optimized to have efficient spray process.

## Phase 2

## Deposition and Characterisation of $Bi_2S_3$ thin films

Bismuth sulphide ($Bi_2S_3$) thin films are deposited by nebulised spray pyrolysis technique. Bismuth nitrate and thiourea are used as the precursor for 'Bi' and 'S' respectively. Substrate temperature is singled out as the variable parameter for the deposition of thin films. Films are deposited at different substrate temperatures (250° C, 300° C, and 350° C). A substrate temperature of 300° C is found to be optimum for the deposition of $Bi_2 S_3$ thin films. Samples are annealed at 300°C. Microscope glass slides and Pilkington FTO glass are used as the substrate for the deposition of $Bi_2S_3$ thin films. Thickness of the films is measured using stylus profilometer. The deposited films are characterized by X-ray diffraction, Energy dispersive X-ray Analysis, Atomic Force Microscopy, UV-Vis spectroscopy, Photoluminescence Spectroscopy and Resistivity measurement. The ECPV cell formed with the $Bi_2S_3$ thin film of lowest resistivity is characterised by C-V and I-V measurements.

### X-ray Diffraction

The structural properties of the annealed (300°C) $Bi_2S_3$ thin films are analysed by X-ray diffraction. The film deposited at a substrate temperature of 300°C exhibited improved crystallinity when compared the films prepared at a substrate temperature of 250°C and 350°C. The diffraction peaks are indexed by comparing the peak positions with the standard data (JCPDS card no.43-1471). The films possessed orthorhombic crystal structure. No peaks corresponding to 'Bi' and 'S' are present thereby indicating that the material is of single phase. Microstructural parameters such as grain size, micro strain and dislocation density are calculated from the XRD data. The grain size is calculated from the diffraction peak broadening using Scherrer relation. Films deposited at a substrate temperature of 300°C consisted of larger grains. The size of the grains in the films deposited at different temperature is in the range 15-20 nm.

### Energy Dispersive X-ray Analysis

The elemental composition of the films are analysed by EDAX. The $Bi_2S_3$ thin films deposited at 300°C are stoichiometric while the films deposited at 250°C and 350°C exhibited slight deviation from the stoichiometry. The EDAX analysis reveals

that a substrate temperature of 300°C is optimum for obtaining stoichiometric $Bi_2S_3$ thin films.

**Atomic Force Microscopy**

Surface morphology and roughness of $Bi_2S_3$ thin films are analysed by atomic force microscopy. The roughness of the films is found to depend on the grain size. The films consisting of larger size have higher RMS roughness and vice-versa. The RMS roughness of the films is in the range of 0.1-7nm.

**UV-Vis-NIR Spectroscopy**

The optical transmittance of the films is analysed using UV-Vis spectroscopy. Optical transmittances of the films are recorded in the range of 300-1200 nm. The transmittance of the films falls of rapidly in the wavelength range of 900-850 nm. The films deposited at 250°C are more transparent than the films deposited at 300°C and 350°C, which may be attributed to the difference in thickness of the films. Optical constants such as absorption coefficient and band gap are calculated from the transmittance data. The films exhibited high absorption coefficient of the order of $10^6$ $m^{-1}$ in the visible region. The optical transitions taking place in the film are found to be direct and allowed. The band gap of the films deposited at different substrate temperature is in the range of 1.4-2.1 eV.

**Photoluminescence Spectroscopy**

Photoluminescence spectrum of the film exhibits a peak at 728 nm which corresponds to the band to band transitions taking place in the films. Absence of any other peaks rules out the possibility of intraband transitions.

**Electrical Resistivity Measurement**

The d.c. electrical resistivity of the films is measured by four probe technique. The d.c. electrical resistivity of the films is recorded at different temperatures. Resistivity of the films decreased with increasing temperature thereby indicating the semiconducting nature of the films. The Arrhenius plots of the samples are linear. The room temperature resistivity of the films deposited at different substrate temperatures is in the range of 8.4 - 4 MΩ. The films deposited at a substrate temperature of 300°C exhibited the lowest resistivity which can be attributed to the improved grain size.

### C-V Measurement

C-V measurement is carried out by forming a three electrode electrochemical cell with the configuration $Bi_2S_3$/1M NaOH-1M $Na_2S$-1M S/C in which calomel electrode and platinum electrode served as the reference and counter electrode respectively. The space charge layer capacitance of the junction as function of applied potential is recorded using an LCR meter. The space charge layer capacitance is found decrease with applied potential. The Mott-Schottky plot of the sample is linear and has negative slope there by indicating the n-type conductivity of the film. Flat band potential is determined by extrapolating Mott-Schottky plot to C=0. Flat band potential of ECPV cell formed with $Bi_2 S_3$ thin film is – 0.6V ($V_{SCE}$).

## Phase 3

### Deposition and Characterisation of $(Bi_{1-x}Sb_x)_2S_3$ thin films

The $(Bi_{1-x}Sb_x)_2S_3$ thin films are deposited by nebulised spray pyrolysis under optimized deposition conditions. Substrate temperature of 300°C is found to be optimum for the deposition of $Bi_2S_3$ thin films and hence $(Bi_{1-x}Sb_x)_2S_3$ thin films are deposited at a substrate temperature of 300°C using $SbCl_3$ as the source of antimony in addition with Bi and S precursors. The ternary films are deposited varying the weight percentage of bismuth and antimony. The value of x is carefully chosen as 0.01<=x<= 0.1. Samples are annealed at 300°C. Microscope glass slides and Pilkington FTO glass are used as the substrates for the deposition of $(Bi_{1-x}Sb_x)_2S_3$ thin films. Thickness of the films is measured using stylus profilometer. The deposited films are characterized by X-ray diffraction, Energy dispersive X-ray Analysis, Atomic force Microscopy, UV-Vis-NIR Spectroscopy, Photoluminescence Spectroscopy, Resistivity and Hall Effect measurements.

#### X-ray Diffraction

The structural properties of the annealed (300°C) $(Bi_{1-x}Sb_x)_2S_3$ thin films are analysed by X-ray diffraction. The diffraction peaks are indexed by comparing the peak positions with the standard data (JCPDS card no.43-1471). The films possessed orthorhombic crystal structure. No peaks corresponding to ‘Bi’, ‘Sb’ and ‘S’ are present thereby indicating that the film is of single phase. The crystallinity of the films is found to decrease with increase in the value of ‘x’. The position of the

prominent peak (130) successively shifts towards higher angles as the value of ‘x’ increases. Microstructure parameters such as grain size, micro strain and dislocation density are calculated from the XRD data. The grain size is calculated from the diffraction peak broadening using Scherrer relation. Films deposited at lower values of ‘x’ consisted of larger grains and vice versa.

**Energy Dispersive X-ray Analysis**

The elemental composition of the $(Bi_{1-x}Sb_x)_2S_3$ films are analysed by EDAX. The films are nearly stoichiometric and a slight sulphur deficiency is observed in films as the value of x increases. The EDAX analysis reveals that a substrate temperature of 300°C is suitable for the deposition of $(Bi_{1-x}Sb_x)_2S_3$ thin films.

**Atomic Force Microscopy**

Surface morphology and roughness of the $(Bi_{1-x}Sb_x)_2S_3$ thin films deposited by nebulised spray pyrolysis are analysed by atomic force microscopy. The roughness of the films is found to depend on the grain size of the films. The roughness of the films is found to decrease with increase in the value of ‘x’ which may be due to the reduction in the crystalline quality of the films.

**UV-Vis-NIR Spectroscopy**

The optical transmittance of the $(Bi_{1-x}Sb_x)_2S_3$ films is analysed using UV-Vis spectroscopy. Optical transmittance of the films is recorded in the range of 300-1200 nm. The transmittance of the films falls of rapidly in the wavelength range of 850-800 nm. Optical constants such as absorption coefficient and band gap are calculated from the transmittance data. The absorption edge of the film shifts towards shorter wavelength with the increase in the value of x. The direct optical band gap of the films is in the range of 1.6-2.2 eV.

**Photoluminescence Spectroscopy**

Photoluminescence spectrum of the film exhibits a peak at 728 nm which corresponds to the band to band transitions taking place in the material. Absence of any other peaks rules out the possibility of intraband transitions. Intensity of the PL peak is reduced when compared with the binary films which may be attributed to the reduction in crystalline quality.

**Electrical Resistivity Measurement**

The d.c. electrical resistivity of $(Bi_{1-x}Sb_x)_2S_3$ films is measured by four probe technique. The d.c. electrical resistivity of the films is recorded at different temperatures. Resistivity of the films decreased with increasing temperature thereby indicating the semiconducting nature of the films. The Arrhenius plots of the samples are linear. The room temperature resistivity of the films is in the range of 0.928k Ω -1.2 MΩ. The resistivity of the films initially decreases with the value of 'x' and then increases. The films recorded a minimum resistivity of 0.928 kΩ when x=0.05. Thermal activation energy of the films is calculated by fitting a straight line for the resistivity data. The films with x=0.05 exhibited lowest thermal activation energy. Thermal activation energy of the films is in the range of 0.1-1.09eV.

**Hall Effect Measurement**

The carrier concentration and Hall mobility of the carriers of low resistivity samples are calculated from Hall measurement. The conductivity type of $(Bi_{1-x}Sb_x)_2S_3$ thin films is determined from Hall measurements. The negative Hall coefficient indicated that the films are n-type semiconductors. Maximum carrier concentration of $3.495x10^{19}$ is recorded for the film with x=0.05. Hall mobility of the carriers decreases with increase in carrier concentration. The Hall mobility of the carriers is in the range of 11-53 $cm^2$/ V-s.

**C-V Measurement**

C-V measurement is carried out by forming a three electrode electrochemical cell with the configuration $(Bi_{1-x}Sb_x)_2S_3$/1M NaOH-1M $Na_2S$-1M S/C in which calomel electrode and platinum electrode served as the reference and counter electrode respectively. The space charge layer capacitance of the junction as function of applied potential is recorded using an LCR meter. The space charge layer capacitance is found decrease with applied potential. The Mott-Schottky plot of the sample is linear and has negative slope there by indicating the n-type conductivity of the material. Flat band potentials of the film are determined by extrapolating Mott-Schottky plot to C=0. Flat band potential of ECPV cells formed with $(Bi_{1-x}Sb_x)_2S_3$ thin films initially decreases with increase in the value of 'x' and then increases. The flat band potential is more positive for the film with x=0.05.

## Phase 4

### Formation and Characterisation of electrochemical photovoltaic cell

Formation and Characterisation of electrochemical photovoltaic cell with $Bi_2S_3$ photoanodes

The thin film of $Bi_2S_3$ is employed as a photoanode in an electrochemical photovoltaic cell with the configuration $Bi_2S_3$/1M NaOH-1M $Na_2S$-1M S/C. Platinum is used as the counter electrode and 1M NaOH-1M $Na_2S$-1M S is used as the electrolyte. The power output characteristic of the cell is studied by illuminating the cell with a radiation of intensity 20 $mW/cm^2$ . The cell parameters such as Voc , Isc, $\eta$, FF, calculated from power output characteristics. Typical values of FF and $\eta$ are 0.5125 and 0.00271 respectively.

Formation and Characterisation of electrochemical photovoltaic cell with

$(Bi_{1-x}Sb_x)_2S_3$ photoanodes

The thin films of $(Bi_{1-x}Sb_x)_2S_3$ are employed as a photoanodes in an electrochemical photovoltaic cell with the configuration $(Bi_{1-x}Sb_x)_2S_3$/1M NaOH-1M $Na_2S$-1M S/C. Platinum is used as the counter electrode and 1M NaOH-1M $Na_2S$-1M S is used as the electrolyte. The power output characteristic of the cell is studied by illuminating the cell with a radiation of intensity 20 $mW/cm^2$ . The cell parameters such as $V_{oc}$ , $I_{sc}$, $\eta$, FF, calculated from power output characteristics. Typical values of FF and $\eta$ are 0.5839 and 0.01345 respectively.

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